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Theoretical Study of Temperature dependent Enthalpy of Absorption, Heat Capacity, and Entropy changes for Protonation of Amines and Amino acid Solvents.

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Abstract

The equilibrium constants for protonation of amine and alkanolamine solvents for post combustion CO_2 capture are studied in this work using density functional theory coupled with the continuum and explicit solvation shell model introduced by da Silva et al. [da Silva, E. F.; Svendsen, H. F.; Merz, K. M. *J. Phys. Chem. A.* **2009**, 113, 6404]. The temperature dependency of the protonation equilibrium constants is very crucial in understanding the thermodynamics of any solvent for post combustion carbon capture. Theoretically calculated temperature dependent protonation equilibrium constants for CO_2 capture solvent are given as input to the Gibbs Helmholtz equations to calculate thermodynamic data of a particular solvent. From the comparison of calculated results from molecular modeling with experimental results, it has been seen that the errors are within experimental error bars.

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Keywords: Heat of absorption, equilibrium constants, Temperature, Amine, Amino Acid, PCM, SM8T, DFT. CO_2 capture.

1. Introduction

Aqueous solutions of alkanolamines are common solvents used for post combustion capture (PCC) of CO_2 from flue gases.[1] Alkanolamines are widely used for gas sweetening processes because they have very high selectivity for acid gases such as CO_2 and H_2S.[2] The first recommendation for usage of amines as chemical solvents for acid gas scrubbing was given by Bottom et al.[3] There is lot of research going on to make the post combustion CO_2 capture process more economical and industrially feasible.[1,4] The knowledge of thermodynamics and energetics of a particular alkanolamine solvent can help in making this process more economical.[4]

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The enthalpy of solution and heat capacity are among the most important properties required for design of CO_2 removal plants. If the enthalpy of absorption of a particular solvent is too low, then it would not be able to capture CO_2 efficiently. On the other hand, if the enthalpy of absorption of CO_2 is too high, it would capture CO_2 efficiently but it would have high energy demands in the regeneration step because of accompanying high heats of desorption. All solvents with high heat of regeneration are not unsuitable for a process, as the performance of a solvent also depends upon its equilibrium temperature sensitivity, which improves with increasing heat of absorption, and the process conditions[5,6]. Hence accurate knowledge of the heat of absorption of a solvent under process conditions is necessary for selecting a particular solvent for industrial CO_2 capture processes.
In this work temperature dependent equilibrium constants for protonation reactions are given as input to the Gibbs Helmholtz equation. By differentiating Gibbs Helmholtz equation, temperature dependent enthalpy, heat capacity and entropy are calculated. Another aim of present work is to apply Gibbs Helmholtz equation to demonstrate thermodynamic consistency of computationally calculated and experimentally derived values.

2. Method

Chemical absorption of CO_2 in amine solutions involves the following reactions

$$CO_2 + R_2NH + B \leftrightarrow R_2NCO_2^- + BH^+, \quad K_{Rxn} \tag{1}$$

$$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+, \quad K_2 \tag{2}$$

$$BH^+ + H_2O \leftrightarrow B + H_3O^+, \quad K_3 \tag{3}$$

$$HCO_3^- + R_2NH \leftrightarrow R_2NCO_2^- + H_2O, \quad K_4 \tag{4}$$

Reaction 3, protonation of amines and amino acids is studied in the present work. If the mole fraction based activity of water for simplicity is assumed to be 1 and if H_3O^+ is written as H^+ the following equilibrium constant can be written for equation (3)

$$K_3 = \frac{a_B a_{H^+}}{a_{BH^+}} \tag{5}$$

The temperature dependency of the equilibrium constants and the Henry's law constant can be expressed in the form[7]

$$\ln K = A + \frac{B}{T} + C \ln T + DT + ET^2 \tag{6}$$

We know that free energy of reaction can be expressed as

$$\Delta G_r = -RT \ln K \tag{7}$$

Combining the well-known Gibbs Helmholtz equation[8] with equations 6 and 7, the enthalpy of the overall reaction can be expressed as

$$T^2 \left[\frac{\partial(\Delta G_r/T)}{\partial T}\right]_P = -\Delta H_r = -RT^2 \left(\frac{\partial lnK}{\partial T}\right)_P = -R(-B + CT + DT^2 + 2ET^3) \tag{8}$$

Differentiation of the obtained temperature dependent enthalpy w.r.t temperature gives the temperature dependent heat capacity, expressed by following equation

$$\Delta C_p = \frac{d(\Delta H_r)}{dT} = -R(C + 2DT + 6ET^2) \quad (9)$$

3. Computational Details

The conformers of the molecules studied were optimized in Spartan 08 using AM1 and DFT level of theory. Conformer search was done in gas phase and in solution phase separately to ensure that we obtain minimum energy structures for further calculations in each phase. In this work, gas phase geometries of alkanolamines and amino acids were fully optimized at the B3LYP level of theory using the 6-311++G (d, p) basis set. Gas phase optimization was carried out in Spartan 08. [9] Frequency calculations confirmed absence of any imaginary frequencies in the minima.

Aqueous phase geometries were fully optimized at B3LYP level of theory using 6-311++G (d, p) functional in Spartan 08 for PCM and SM8T calculations using solvent model SM8. Single point energy calculations on the optimized geometry of the molecule obtained were used to study the solvation effects with the SM8T solvation models. SM8T calculations[10] were done in Gamessplus[11] for the temperature range 273.15 - 373 K using the optimized structure obtained earlier. All SM8T calculations were done using Density Functional Theory at SM8T/B3LYP/6-311++G (d, p)//SM8/B3LYP-6-311++G (d, p) level. The solvation free energy of the protonated alkanolamines were also calculated by the explicit solvation shell model, (ESS), introduced by da Silva et. al.[12]. Full details for extracting the solvation shell geometries from molecular simulations and further details of the model can be found in Gupta et al.[13]

4. Results and Discussion

Determining equilibrium constants for reaction 3, i.e the deprotonation of the solvent, comprises the calculation of gas phase and solution phase thermodynamics of the amine or amino acid and their protonated counterparts. Gas phase calculations carried out at DFT level of theory are shown to give good results for amine and amino acid functionalities[13]. However, in solution phase the situation is not very satisfactory and we observe large errors in solvation free energies of ions, i.e protonated amines and amino acid solvents. The explicit solvation shell model is used in this work for the calculation of free energy of solvation of protonated counterparts of molecules. The explicit solvation shell model is shown to give more accurate results for ions[13]. An optimized cluster for PZ having 5 explicit water molecules obtained from molecular simulations using ESS is shown in Fig. 1. Similar clusters for all optimized molecules were obtained using ESS in this work.

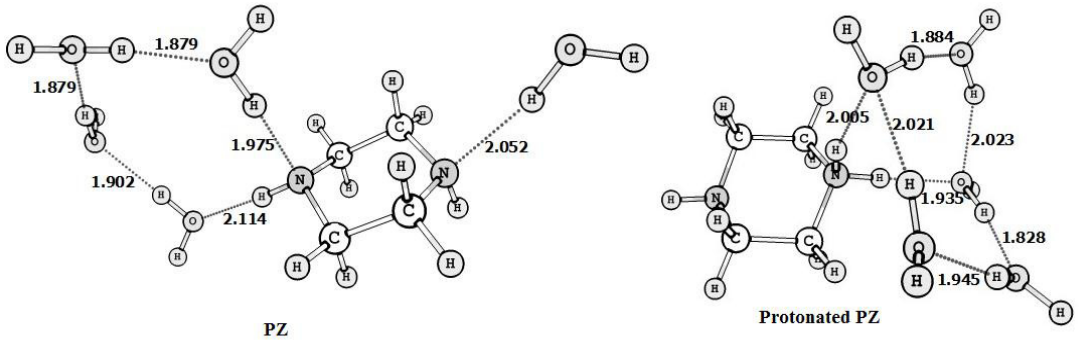

Fig 1: Most Stable ESS clusters obtained for PZ and protonated PZ. (The dotted lines show the hydrogen bonding in the molecule, and the bond lengths of the hydrogen bonds are also given in angstroms).

Gas phase and solution phase geometries of protonated and neutral molecules were fully optimized at the B3LYP level of theory using the 6-311++G (d, p) basis set. Fully optimized structures of neutral and protonated MEA and MDEA are shown in Figure 2 in gas phase. A similar optimization procedure was employed for the full set of amines and amino acid molecules studied in the present work.

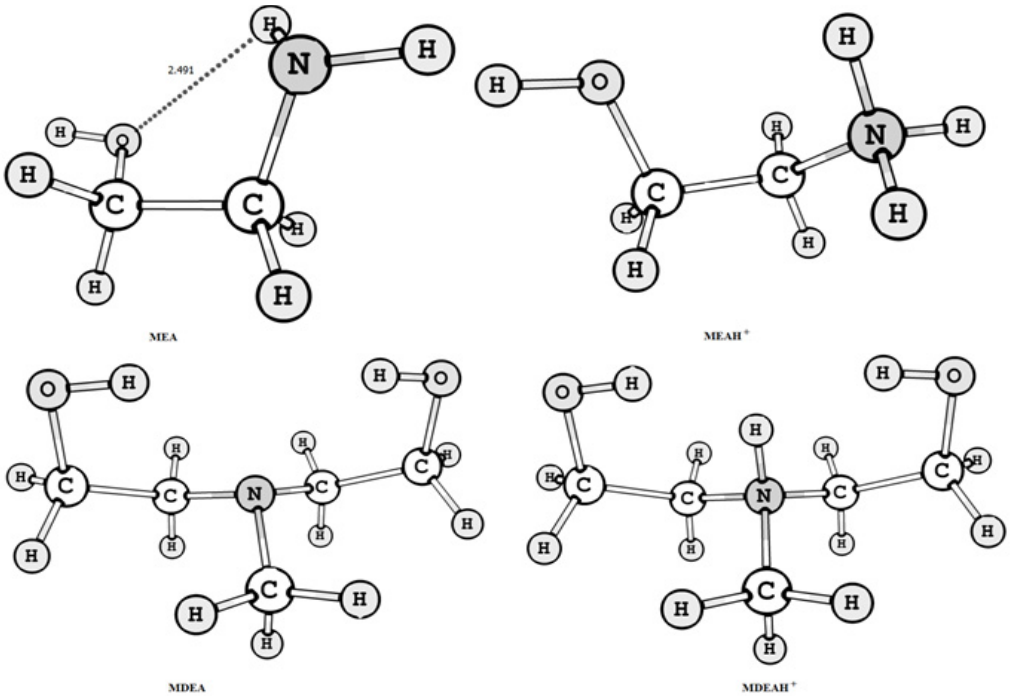

Fig 2: Most Stable conformers of MEA, protonated MEA, MDEA and protonated MDEA. (The dotted lines show the hydrogen bonding in the molecule, and the bond lengths of the hydrogen bonds are also given in angstroms).

In this work the temperature dependent enthalpy of absorption and heat capacity of protonation reaction for a set of amines and amino acids were studied using equations 6-9 given above. We have calculated the heat of absorption based on correlations for the temperature dependent lnK values for the deprotonation reaction 3. Experimental protonation constants at 298 K were given as input to the computational thermodynamic model[14] used to calculate the temperature dependency of the thermodynamic properties. At 298 K, DFT gaseous phase free energies were coupled with solvation free energies calculated with explicit solvation shell model for calculation of the free energy of protonation in solution. The cases where there was a large discrepancy between calculated and experimental free energy of protonation in solution, the calculated free energy of protonation in solution was shifted to experimental free energy of solution and this difference added to all temperatures.

Figure 3 shows temperature dependent enthalpies of protonation for MEA and Piperazine. The calculated reaction equilibrium constants were used in equation 8 to give enthalpies of protonation and equation 9 gives the temperature dependent heat capacity. Similar calculations were done for the other amines and amino acids. Study of temperature dependent enthalpy of absorption and heat capacity is of great importance as it provides useful information for the performance of different solvents in any temperature swing process such as post combustion CO_2 capture. The calculated results are compared against experimental data.[15-18]

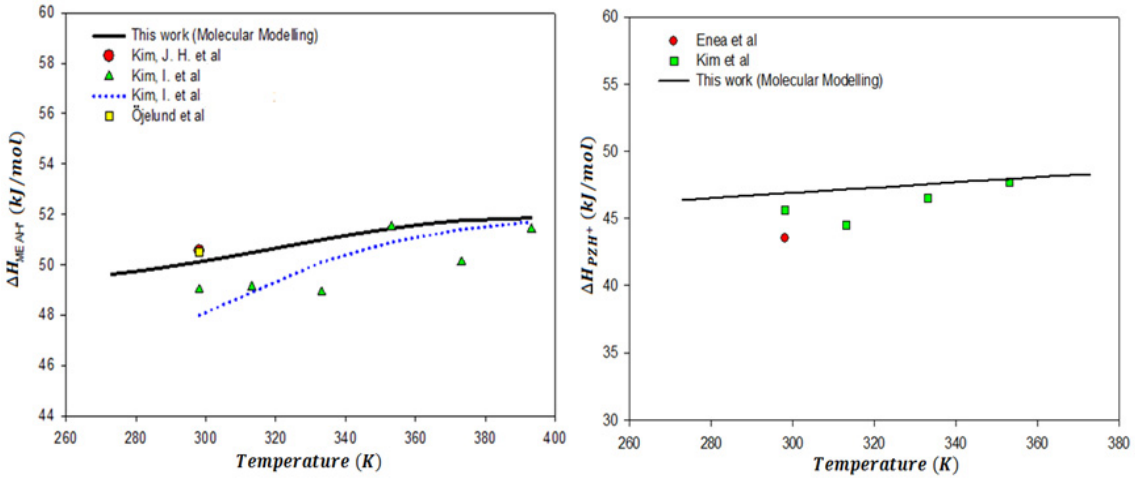

Figure 3: Enthalpies of deprotonation for $MEAH^+$ and PZH^+ as function of temperature from Molecular Modeling compared with available literature data.

In table 1, standard state free energy of protonation (ΔG_r^0), pKa, enthalpy of absorption (ΔH_r^0) and entropy (ΔS_r^0) for alkanolamines and amino acids, calculated in the present work, are given. These thermodynamic values are calculated by taking the average of all the thermodynamic quantities in the temperature range 273 K to 373 K, which are calculated by giving equilibrium constants for the deprotonation reaction from molecular modelling as input to Gibbs Helmholtz equation 8.

Table 1: Free energy of protonation (ΔG_r^0), pKa, enthalpy of absorption (ΔH_r^0) and entropy (ΔS_r^0) for alkanolamines and amino acids calculated in the present work.

S.No.	Compound	Name	ΔG_r $(\frac{kJ}{mol})$	pKa	ΔH_r $(\frac{kJ}{mol})$	ΔS_r $(\frac{J}{K*mol})$
1	MEA	Ethanolamine	55.46	9.44	46.81	-29.0
2	PZ (pKa2)	Piperazine	57.01	9.71	41.01	-53.7
3	PZ (pKa1)	Piperazine	32.43	5.41	30.51	-6.4
4	β–ala	β–alanine	60.51	10.33	45.01	-52.0
5	MDEA	N-methyldiethanolamine	50.40	8.62	32.91	-58.7
6	AEPD	2-amino-2-ethyl-1,3-propanediol	51.88	8.82	45.71	-20.7
7	AMP	2-amino-2-methylpropanol	56.80	9.68	50.41	-21.4
8	DEMEA	diethylmonoethanolamine	57.20	9.75	34.41	-76.5
9	DIPA	diisopropanolamine	52.03	8.84	37.41	-49.1
10	DMMEA	dimethylmonoethanolamine	54.19	9.22	32.61	-72.4
11	MIPA	1-amino-2-propanol	55.50	9.45	47.01	-28.5
12	MMEA	Monomethylethanolamine	57.76	9.85	42.61	-50.8
13	tau	Taurine	53.25	9.06	39.71	-45.4
14	sar	sarcosine	59.83	10.21	37.91	-73.6
15	6-AHA	6-aminohexanoic acid	64.05	10.8	54.71	-31.3

Heat capacities for alkanolamines and amino acids calculated in the present work are given in Table 2. The heat capacity of a solvent calculated in this work, shows very low temperature dependency. Experimental heat capacity is also shown to vary very little with temperature.

Table 2: Heat capacities (ΔC_p) for alkanolamines and amino acids calculated in the present work.

S.No.	Compound	Name	ΔC_p $(\frac{J}{K*mol})$
1	MEA	Ethanolamine	82.3
2	β–ala	β–alanine	-10.1
3	MDEA	N-methyldiethanolamine	86.3
4	AMP	2-amino-2-methylpropanol	110
5	DIPA	diisopropanolamine	135
6	tau	taurine	-22.7
7	sar	sarcosine	-1.7
8	6-AHA	6-aminohexanoic acid	25.8

The thermodynamic values given in Table 1 and 2 for alkanolamines and amino acids studied in this work are within experimental error bars.

5. Conclusions

Derived correlations are compared with available experimental enthalpy and heat capacity data at infinite dilution and shown to be thermodynamically consistent. We obtained overall temperature dependent enthalpy and heat capacity of protonation of amines and amino acid solvents having potential for PCC solvents. The results from this work may be used for thermodynamic modeling of CO_2 capture processes using alkanolamine and amino acid solvents.

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